

High Density Hydrogen Storage System Demonstration Using NaAlH₄ Based Complex Compound Hydrides

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Objectives

- Improve the charging and discharging rates of the NaAlH₄ based hydrogen storage medium. Specifically, in collaboration with other efforts:
 - Increase the reversible weight fraction of hydrogen stored to 7.5% from the current 5.5%
 - Enhance the hydrogen evolution rate from 0.1 wt%/hr at 80°C to 0.55 wt%/hr to meet fuel cell demands
 - Increase the regeneration rates from the documented 0.5 wt%/hr to 90 wt%/hr to achieve the five minute refill requirement
- Determine the safety and risk factors associated with enhanced compositions
- Design, develop and evaluate a hydrogen storage system having a 5 kg hydrogen capacity and installation capability in a fuel cell powered mid-size sedan

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight & Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Create combined atomistic/thermodynamic models of the NaAlH₄ system to determine catalyzed compositional ranges, sorption mechanisms and the effects various catalyst additions have on these mechanisms.
- Cyclically evaluate selected Complex Compound Hydride (CCH) compositions to determine degradation mechanisms and ameliorations as well as compatibility with construction materials.
- Conduct standardized safety testing related to the classification of hazardous materials.

- Develop preliminary designs through the evaluation of existing systems, generation of weight/volume/cost improvements, and high level optimization to balance automotive demands.
- Perform heat and mass flow modeling for detailed optimization of the required system volume, mass and hydrogen sorption characteristics. Evaluate methods to enhance heat conduction into the CCH powder.
- Fabricate and evaluate 1 kg H₂ and 5 kg H₂ capacity hydrogen supply systems.
- Conduct preliminary system performance modeling analyses of the combined proton exchange membrane fuel cell (PEMFC)/H₂ storage system under steady state and transient conditions to establish system optimization and dynamic control requirements.

Accomplishments

- Applied atomistic/thermodynamic modeling to complex compound hydrides successfully.
- Completed safety experiments resulting in no change in transportation packing class for these materials from their unmodified condition.
- Characterized two alanate compositions for sorption kinetics.
- Identified preliminary design and materials of construction based on volume, mass and cost estimates.
- Completed sub-component models and trials.

Future Directions

- Complete design of the first 1 kg hydrogen storage system designated CCHS#1.
- Identify catalyzed NaAlH₄ media composition from characterized compositions.
- Complete fabrication, media catalyzation and loading of CCHS#1.
- Evaluate system operating characteristics, hydriding and dehydriding rates, and system volumetric and gravimetric densities utilizing laboratory supplied heat and hydrogen.
- Initiate system modeling efforts based on previously understood fuel cell and balance-of-plant models.

advantages and disadvantages, but none is clearly superior for automotive transportation. In particular, a disadvantage of metal hydrides is their low hydrogen capacities of less than 2 wt% for alloys with discharge temperatures such that the waste heat of a PEMFC (~ 90 °C) can be used to release the hydrogen. Many chemical hydride materials, while having high capacities, are classified as irreversible, which requires that the entire material be replaced during refueling rather than simply charged with hydrogen gas. This project is focusing on the reversible chemical hydride, NaAlH₄, with a theoretical hydrogen capacity of 5.5 wt%, and seeks to enhance the material for improved charging and discharging rates as well as increased capacity. Safety studies of the enhanced material will be conducted to support the technology as it is driven toward commercialization.

Introduction

One of the most significant barriers to the widespread application of hydrogen-based propulsion is the development of on-board storage systems which can provide the needed quantity of hydrogen with acceptable volume, weight, cost and safety risk. The major classes of established hydrogen storage methods - compressed gas, liquid, metal hydrides and chemical hydrides - all have

The project also seeks to apply this material in the development of a system which will reversibly store a high wt% of hydrogen at low pressure for an indefinite amount of time. The storage system which contains the CCH powder must serve two primary functions: (1) exchange heat between the powder and a working liquid to drive the absorption/desorption of hydrogen; (2) support elevated hydrogen pressure during refueling. These functions must be performed

with a minimum of weight, volume and cost. In addition, there are other secondary characteristics such as (i) allowing for significant volumetric change of the powder, (ii) exchanging hydrogen without the loss of the fine CCH powder particles, (iii) maintaining chemical compatibility with the CCH powder and hydrogen, (iv) producing minimal impurities going to the PEMFC, and (v) fitting into a conformable volume.

Approach and Results

Atomistic models were created utilizing the Vienna Ab-initio Simulation Package (VASP) of NaAlH_4 , Na_3AlH_6 and NaH using known lattice parameters and atomic occupation sites. Full volume and site relaxations were allowed with resulting structures nearly identically replicating literature values. Catalyst substitutions of Ti^{+3} , V^{+3} , Zr^{+4} and Li^{+1} were made in both the NaAlH_4 and Na_3AlH_6 structures with transition metal substitution for Al^{+3} cations and alkaline metal substitutions for Na^{+1} cations showing the lowest lattice energy, by far (see Figure 1). Lattice enthalpy (DH) calculations were performed on various "compositions" of catalysts from which thermodynamic calculations utilizing ThermoCalc were able to determine free energy of formation, DG. From the free energy determinations, the vant Hoff plots for various compositions of catalyst were calculated, see Figure 2. The results of these calculations indicate catalyst additions modify the thermodynamics of hydrogen sorption and thus play a far more significant role than simple heterogeneous catalysis as referred to in the literature.

An equation depicting the rate of a chemical reaction as a function of temperature, pressure and composition taken from Reference 1 which was first implemented in modeling of LaNi_5 hydrogen storage beds is defined as:

$$\left(\frac{dC_1}{dt}\right)_{r1} = A_1 \exp\left(-\frac{E_1}{RT}\right) * \left(\frac{P_{e,1} - P}{P_{e,1}}\right) * (C_2)^{x_1}$$

where C_i is the composition; $P_{e,i}$ is the plateau pressure for composition i ; A_i , E_i and C_i are experimentally determined constants for reaction i ; and t , R , T and P are the time, gas constant,

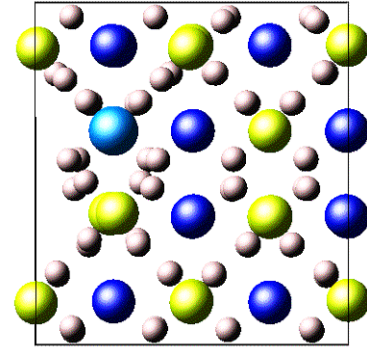


Figure 1. Atomistic Model Depicting Insertion of Ti^{+3} Cation into NaAlH_4 Super-Cell Substituting for Al^{+3} Cation after Volume and Energy Relaxation

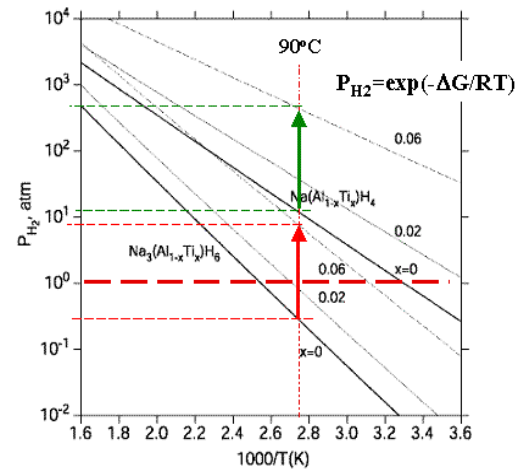


Figure 2. Vant Hoff Plot of Calculated Pressure Equilibria for 2 & 6 m% Ti^{+3} Substituted NaAlH_4 and Na_3AlH_6

temperature, and pressure, respectively. Figure 3 depicts the modeled rates of reaction and experimental verification of the model with very good agreement resulting. These equations can be solved simultaneously for the sorption rates of NaAlH_4 and Na_3AlH_6 respectively. Given these rates of reaction and the heats of reaction developed elsewhere, a spatially resolved temperature distribution can be modeled utilizing a finite element method (FEM) code. These calculations were carried out using various preliminary system designs, heating fluid temperatures, etc. Figure 4 shows the results of three such simulations for differing numbers of heat transfer fluid conduits.

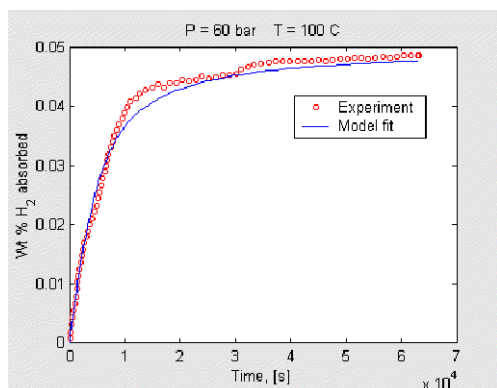


Figure 3. Comparison of Calculated and Measured Hydrogen Absorption and Desorption

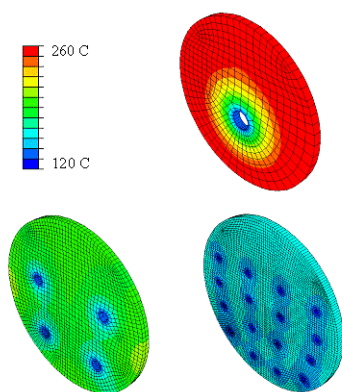


Figure 4. Temperature Distribution at 1400 sec. after Charging at 100 Bar H_2

A series of experiments were conducted to measure the reactivity of the catalyzed CCH media in contact with either water or air. Experimental details were taken from two sources: DOT/UN Doc., Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria [Reference 2], and from ASTM E1226, Dust Explosion Testing. Tests were conducted in three materials states: fully charged, primarily $NaAlH_4$; partially discharged, composed of a mixture of Na_3AlH_6 and Al^0 powder; and fully discharged, composed of NaH and Al^0 powders. Various combinations of water and air contact and ambient and elevated temperatures were included in the testing protocols. The results of these tests confirmed that these compounds are water and humidity reactive, but their packaging and handling classifications do not change with the addition of

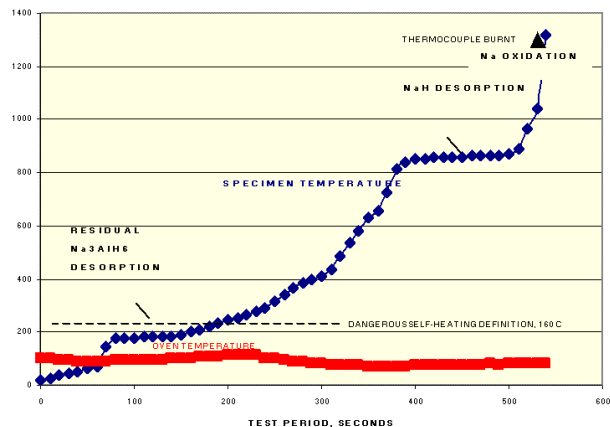


Figure 5. Time/Temperature Plot of Partially Discharged Material Heated to 100°C in Air Showing Various Oxidation Events

catalysts. The hexa-hydride materials were somewhat more reactive in spontaneous ignition and burn rate testing than either of the other compositions.

The results of one test are depicted in Figure 5 where the partially discharged material was packed into a 25 cm³ cube, loaded into a furnace and heated in air to 100°C. The temperature vs. time plot given in Figure 5 shows the development of oxidation reactions in which a thermocouple is inserted into the powder. Two reactions are clearly observed, one initiating at approximately 200°C which is thought to be dehydrogenation of the Na_3AlH_6 compound, and the other initiating at ~850°C thought to be dehydrogenation of NaH . Oxidation of Na^0 and Al^0 metals proceeds exothermically to temperatures greater than 1200°C where the thermocouple failed.

Conclusions

1. Numerous experiments were carried out on catalyzed $NaAlH_4$ in various phases of decomposition. The results indicate these materials to be flammable when in contact with water or water vapor in the air. The partially discharged material containing a mixture of Na_3AlH_6 and aluminum powder was found to be somewhat more reactive than the fully charged material, but in all cases, the packing classification did not change.

2. Significant advances have been made in modeling of the media utilizing a combination of atomistic and thermodynamic methods which has proven to be state-of-the-art in its methodology and enlightening in its results. If the catalytic additions can be made to stay within the host structure, upon repeated sorption cycles, the full 5.5 wt% of hydrogen should be accessible at pressures above 1 bar.
3. An analytical expression for hydrogen sorption rates was identified in the literature and utilized in conjunction with known thermodynamic values to predict temperatures in simulated hydrogen storage systems.

References

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5. D.L. Anton, *Hydrogen Desorption Kinetics in Transition Metal Modified $NaAlH_4$* , J. Alloys & Compounds, (in press).
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